

离舌囊吾中一新三萜皂甙——离舌囊吾甙 A

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LIGUVEITOSIDE A, A NEW TRITERPENOID SAPONIN FROM LIGULARIA VEITCHIANA

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In our previous paper, we reported two new eremophilane derivatives from *Ligularia veitchiana*^[1]. Further research to the polar section of this plant led to the isolation of a new triterpenoid saponin, named Liguveitoside A. Its structure was determined on the basis of the spectral and chemical methods.

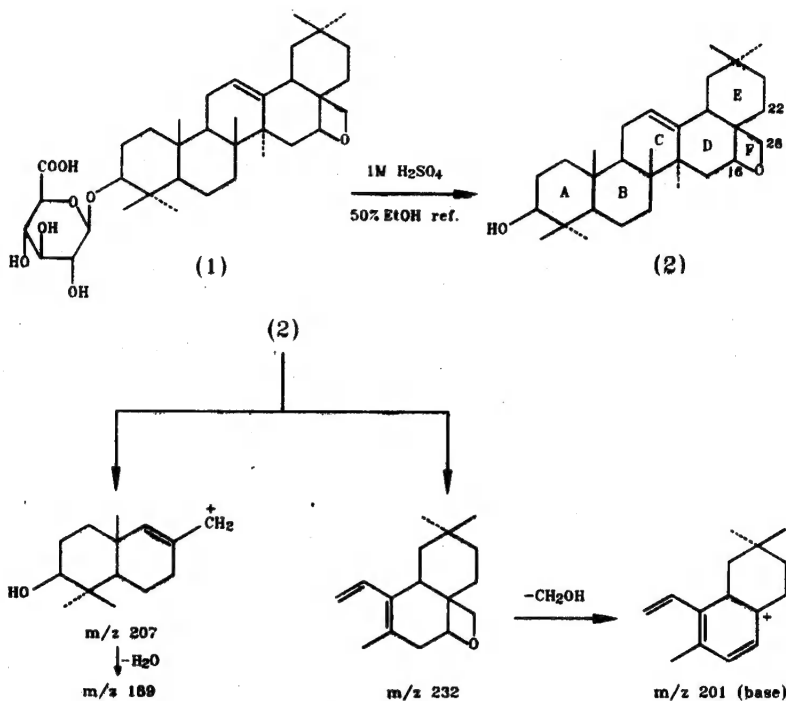
Liguveitoside A (1) was obtained as colorless needles, with a m. p. at 220—221°C, from the n-BuOH soluble part of the EtOH extract of the plant. Comparison of the ¹³C NMR spectrum of 1 with those of the reported saponins^[2] revealed that Liguveitoside A was an oleanane-type monodesmoside. The molecular formula of 1 (C₃₆H₅₆O₈) was concluded from the peak at m/z 617 [M+H]⁺ in the positive FAB mass spectrum, while its fragment ion peaks were exhibited at m/z 439 [M-GlcUA]⁺ and 423 [M-OGlcUA]⁺, suggested the presence of a glucuronic acid piece in the molecule. Acid hydrolysis of 1 gave glucuronic acid (detected by PC), and the aglycone (2).

Compound 2 was analysed for seven tertiary methyls (δ 0.73—1.16, 21H, 7×Me), one -CH₂O- group (an AB system at δ 3.13 and 4.11, 1H each, a pair of doublets, J_{AB} = 10.8 Hz), one olefinic proton (δ 5.13, t, J = 3.5 Hz) and two oxygen-bearing methine protons (δ 3.17, dd, J = 10.0, 3.7 Hz; δ 4.24, ddd, J = 9.9, 2.4, 1.7 Hz). The EI mass spectrum of 2 showed a series of diagnostically important mass peaks at m/z 207, 189(207-H₂O), 232 and the base peak at m/z 201 (232-CH₂OH), which were typically attributed to a retro Diels-Alder fragmentation of an olean-12-en derivative bearing one hydroxy group in rings A/B^[3].

Furthermore, a double doublet at δ 3.17 in the ¹H NMR spectrum of 2 with coupling constants at J = 1.0 Hz (axial-axial coupling) and J = 3.7 Hz (axial-equatorial coupling) corresponded to 3 α -H(axial

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proton), showed the equatorial orientation of the hydroxy group at C-3. According to the unsaturated value of **2**, another ring(named F ring) was most likely to exist in compound **2**. This ring was finally deduced to be a four-membered ring, formed by connection of C-28 and C-16 through an ether link. This could be evidenced by the ^{13}C NMR spectrum of **2**, for the chemical shifts of C-28 and C-16 was somewhat upfield shifted (by γ -effects each other) when comparing with the ^{13}C NMR spectra of the 16-hydroxy derivative and the 28- CH_2OH derivatives ^[4].



Moreover, one of the AB system protons (H-28) was found to be a double doublet ($J = 10.8, 2.4\text{Hz}$), while H-16 at $\delta 4.24$ exhibited as a ddd peak ($J = 9.9, 3.7, 2.4\text{Hz}$), suggested an long distance W-type coupling was present between H-16 and H-28. Shown by the demonstrating model, only an axial orientation of H-16 ($16\alpha\text{-H}$) permits this W-type coupling.

In addition, no variation of C-14 and C-20 in the ^{13}C NMR spectrum of **2** was found when comparing with oleanane-type triterpenoids, also supported the above-mentioned structure.

Liguveitoside A (1): $\text{C}_{36}\text{H}_{56}\text{O}_8$, colorless needles, mp $220\text{--}221^\circ\text{C}$ (MeOH). FAB-MS(positive) (m/z): 617 [$\text{M}+\text{H}$] $^+$ (36), 439(25), 423(87), 286(75), 273(100), 201(65), 176(84). ^{13}C NMR (δ , CD_5N): 38.90(C-1), 26.31(C-2), 89.11(C-3), 40.26(C-4), 55.83(C-5), 18.53(C-6), 34.37(C-7), 41.11(C-8), 47.19(C-9), 36.86(C-10), 23.90(C-11), 122.66(C-12), 144.01(C-13), 43.96(C-14), 36.86(C-15), 66.80(C-16), 39.60(C-17), 44.62(C-18), 47.19(C-19), 31.10(C-20), 33.05(C-21), 26.67(C-22), 28.25(C-23), 16.99(C-24), 15.70(C-25), 16.99(C-26), 27.17(C-27), 69.08(C-28), 33.41(C-29), 24.14(C-30); 107.20(C-1'), 77.80(C-2'), 78.22(C-3'), 73.44(C-4'), 75.59(C-5'), 172.75(C-6').

Liguveitol (2): $\text{C}_{30}\text{H}_{48}\text{O}_2$, colorless gum, EIMS (m/z): 440 [M] $^+$ (92), 423(55), 232(57), 201(100). ^{13}C

NMR (δ , C_5D_5N): 38.63(C-1), 26.21(C-2), 78.73(C-3), 39.78(C-4), 55.22(C-5), 18.32(C-6), 33.58(C-7), 40.11(C-8), 46.76(C-9), 38.77(C-10), 23.46(C-11), 122.30(C-12), 142.98(C-13), 43.67(C-14), 36.04(C-15), 67.52(C-16), 36.84(C-17), 44.72(C-18), 46.64(C-19), 30.73(C-20), 32.56(C-21), 27.18(C-22), 28.08(C-23), 15.52(C-24,25), 16.65(C-26), 26.76(C-27), 70.88(C-28), 33.06(C-29), 23.87(C-30).

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$\Delta\epsilon_{253}$ —1.02(MeOH; c 0.164)表示。

10. NMR 表示为 1H NMR 或 ^{13}C NMR, 须注明仪器的频率, 溶剂及内标物。化学位移以 δ 值(对 TMS)表示, 注明峰形, 如: 单峰(s), 宽单峰(brs), 双峰(d), 双二重峰(dd), 复峰(m)等。 ^{13}C NMR 及 1H NMR 数所须注明所对应的碳和氢的位置, 采用 IUPAC 定位, 标为 C-1, C-2; H-1, H-2。例如: ^{13}C NMR(21.15Mz, $CDCl_3$): δ 30.1(t, C-5), 74.1(d, C-6), 121.3(d, C-3), 144.2(s, C-4)。 1H NMR(100MHz, $CDCl_3$): δ 0.681(3H, s, H-18), 0.884(6H, d, J = 6.0Hz, H-26 and H-27), 0.901(3H, d, J = 5.0Hz, H-21), 4.342(1H, q, $J_{6\alpha}$, 7α = 4.5Hz, $J_{6\alpha}$, 7β = 2.0Hz, H-6), 4.211(1H, m, $W_{1/2}$ = 18.0Hz, H-3 α)。所用仪器频率及溶剂若在实验部分的总论中已注明, 则以下皆可省略。

11. 质谱须注明所用的方法, 如(EIMS, CIMS, GC-MS, FABMS 等)及离解能, 只须给出分子离子峰及重要的特征碎片峰(相对强度), 如: EIMS(70eV m/z (%): 386[M^+](36), 368[$M-H_2O$] $^+$ (100), 275[$M-111$] $^+$ (35)等。高分辨质谱(HRMS)若有必要可多给一些信息。

12. 紫外光谱表示法, 如 $UV_{\lambda_{max}^{EtOH}}nm(lge)$: 203(4.17)。

13. 红外光谱表示法, 如 $IR_{\nu_{max}^{KBr}}cm^{-1}$: 1740。官能团的指定放在圆括号内, 如: 1740(>C=O)。若要标明吸收带的强度, 则采用以下缩写符号: w(弱), m(中等), v(可变), s(强), vs(很强)。

14. 有机化合物和无机化合物及有关的缩写符号须规范化(参考 CA), 如氘代溶剂 $CDCl_3$, $DMSO-d_5$, D_2O , pyridine- d_5 等。常见化学试剂在文中均以化学符号表示, 如: MeOH, EtOH, n -BuOH, PrOH, iso-PrOH, PhOH(苯酚), petrol(石油醚), $CHCl_3$, CCl_4 , C_6C_6 , Et_2O , Me_2CO , HOAc, EtOAc, THF, Ac_2O , NaOMe, CH_2N_2 , HCO_2H (甲酸), TCA(三氯乙酸), TFA(三氟乙酸), NaOAc, NaOH, HCl, H_2SO_4 , CO_2 , H_3BO_3 , NH_3 , N_2 等。

15. 制备薄层析须注明(1)薄层厚度; (2)样品的量; (3)确定带的方法; (4)从吸附剂上洗脱下化合物所用的溶剂。特殊 TLC 的吸附剂须注明, 如: $AgNO_3$ -硅胶(1:9)。

16. 气相色谱(GC)须注明检测器(FID, EC 等), 载气及流速, 操作温度, 柱子情况等。

17. 高压液相(HPLC)须注明(1)柱子情况, 如大小、型号; (2)压力及溶剂; (3)检测方法, 如 UV 或折光率。

18. X-衍射只须给出立体结构图(最好有键长)及必要的数字, 详细记录可指明在什么地方储存。